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MERIDIONAL FLUXES OF DISSOLVED ORGANIC MATTER IN THE NORTH ATLANTIC OCEAN

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Abstract. Using bio-optical estimates of gelbstoff and a few platinum measurements of dissolved organic carbon (DOC_{pt}), a budget of the meridional flux of DOC and dissolved organic nitrogen (DON) across 36°25'N in the North Atlantic is constructed from previous inverse models of water and element transport. Distinct southward subsurface fluxes of dissolved organic matter (DOM) within subducted shelf water, cabelled slope water, and overturned basin water are inferred. Within two cases of a positive gradient of DOC_{pt} between terrestrial/shelf and offshore stocks, the net equatorward exports of O_2 and DOC_{pt} from the northern North Atlantic yield molar ratios of 2.1 to 9.1, compared to the expected Redfield O_2/C ratio of 1.3. In the first case, 63% of the apparent oxygen utilization demands of the water column may be met by DOC, instead of only 14% in the second scenario, preserving a role for falling particles in the sea. With a DOC/DON ratio of 10, the larger net southward export of DON across 36°25'N balances the postulated net northward input of 1.7×10^3 kg NO_3 s^{-1} of unutilized nitrate within the Gulf Stream. Without an enhanced supply of DOM from the shelves, a zero seaward gradient of DOM in the third case suggests that none of the poleward nitrate flux is returned southward as DON, but instead a net poleward flux of DON prevails as well. Our present estimates are confounded, however, by the seasonal and multiyear variability of sinking processes in the North Atlantic. Future active and passive remote sensors, field programs, and simulation models must now discriminate between particulate and dissolved components of surface color signals to verify the importance of both continental margins and DOM in global biogeochemical cycles.

1. Introduction

Recent measurements of dissolved organic carbon (DOC) and nitrogen (DON) in sea water, involving varying amounts of a platinum catalyst [*Suzuki et al.*, 1985, 1992; *Sugimura and Suzuki*, 1988] have rekindled controversies [*Williams and Druffel*, 1988; *Jackson*, 1988], ignited at the turn of the century [*Putter*, 1909], about the roles of dissolved organic matter (DOM) in the ocean. Prior large estimates of DOC in the ocean, obtained with different methods [*Plunkett and Rakestraw*, 1955; *Skopintsev et al.*, 1966; *Gordon and Sutcliffe*, 1973; *Melnikov and Pavlov*, 1978] had been rejected in favor of the lower values obtained with ultraviolet and peroxodisulfuric acid techniques of wet combustion [*Armstrong et al.*, 1966; *Menzel and Vaccaro*, 1964], although unmeasured organic acids could account for differences in potentiometric and manometric estimates of total CO_2 in seawater [*Bradshaw and Brewer*, 1988]. If the even larger values of DOC measured with the platinum technique are correct, they raise questions about prior estimates of regional sources and sinks of the global carbon budget [*Tans et al.*, 1990], particularly in the North Atlantic, which is the subject of our analysis.

Using depth profiles of Apparent Oxygen Utilization (AOU) and the platinum estimates of DOC, 80% [*Toggweiler*, 1989] to 100% [*Sugimura and Suzuki*, 1988] of the respiration in the aphotic zone is now attributed to consumption of DOC, rather than of falling particles in the western Pacific. This hypothesis is a sharp contrast to a previous estimate for the same region [*Ogura*, 1970], which suggested that at most 25% of AOU demands were met by a DOC source, based on a Redfield molar O_2/C ratio of 1.3 [*Redfield et al.*, 1963] and the wet combustion method [*Menzel and Vaccaro*, 1964]. These new findings imply that the global downward flux of DOC may be equivalent to the particulate rain of marine carbon, representing 50-67% of new production in simple models of the open ocean [*Toggweiler*, 1989; *Bacastow and Maier-Reimer*, 1991; *Najjar et al.*, 1992].

Local invasion of most of the deep sea by surface DOM must occur at slower rates than the settling velocities (~100 m d^{-1}) of large particles [*Alldredge and Gotschalk*, 1989], however. At similar rates to those of nitrate infusion up the oceanic nutricline [*Walsh*, 1991], for example, diffusive invasion by surface DOM at a rate of 1 cm^2 s^{-1} is equivalent to a penetration speed of ~37 m yr^{-1} over the upper 100 m of the water column. At this rate, it would take at least 27 years to arrive at a depth of 1000 m; eddy diffusion of DOM across the main pycnocline would be even slower. Over this time, lateral advection, particularly that of western boundary currents (>100 km d^{-1}), may allow pilgrimage of tropical and subtropical DOC pools to polar latitudes [*Toggweiler*, 1989], where convective mixing may accelerate the descent of DOC.

Otherwise, photodegradation [*Keiber et al.*, 1990] and bacterial utilization [*Kirchman et al.*, 1991] of DOC in surface waters may return most of this dissolved form of photosynthate back to the atmosphere as biogenic CO_2, leaving behind a relatively inert component of DOC. The ^{14}C age [*Williams and Druffel*, 1987] and C/N ratio [*Jackson and Williams*, 1985] of deep-sea pools of DOM determined by UV-radiation are 6000 years and 25, for example, instead of the C/N ratios of 5-7 [*Sugimura and Suzuki*, 1988] and a bomb-label [*Druffel et al.*, 1989] for DOC measured with the platinum method. The more recent observations imply a younger and less refractory component of DOC as well, at least in offshore waters [*Kirchman et al.*, 1991; *Suzuki and Tanoue*, 1991; *Benner et al.*, 1992]. In contrast, the radiocarbon age of near-surface humic and fulvic acids, comprising 20-50% of the DOC

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sampled by UV-oxidation [*Harvey et al.*, 1983; *Meyers-Schulte and Hedges*, 1986; *Williams and Druffel*, 1987], is about 4000 years [*Druffel et al.*, 1989].

The identity of these additional labile pools of DOM, if and whether they really exist in soluble, colloidal (0.005-0.050 μm diameter), or fine particle (0.050-1.000 μm) form, remains an unresolved issue [*Benner et al.*, 1992]. Their sources (terrestrial, coastal, and oceanic) and fates (photodegradation, remineralization, and storage as inert forms of DOC) are also open questions, which underscore our inadequate understanding of temporal-spatial variance in the biogeochemical cycles of carbon and nitrogen [*Walsh*, 1991].

To qualify as a dynamic storage reservoir in global carbon budgets [*Tans et al.*, 1990], however, DOM stocks, like those of dissolved inorganic carbon (DIC), must be removed from surface regions of the ocean by sinking water, if not by falling particles, to avoid respiration back to CO_2 at the sea-surface. We explore this mechanism by considering (1) the possible DOC stocks in shelf, slope, and basin regions of the North Atlantic Ocean as estimated with both platinum (DOC_{pt}) and ultraviolet (DOC_{uv}) techniques; (2) their potential annual sinking fluxes in relation to freshwater and photosynthetic supplies; and (3) the implied net southward transfer of subsurface DOC and DON in relation to other meridional fluxes of oxygen and nitrate across 36°25'N.

2. Methods

In a previous study, *Rintoul and Wunsch* [1991] suggested that the net poleward transfer of nitrate by the Gulf Stream System across 36°25'N (the location of this section is shown in Figure 1) might be balanced by a southward transport of DON. *Rintoul* [1988] provides zonally averaged estimates of meridional transport of water over 17 vertical levels (Table 1) at this latitude, based on an inverse model, which conserves both mass and silicate below a depth of 750 m and has a reference level of 3000 dbar. Using their results, we construct budgets of the possible southward export of DOC and DON from the North Atlantic at four of the depth intervals, over which sinking water may exit this basin towards the equator. The net exchange over the whole water column is then obtained by summing the DOC_{pt} and DOC_{uv} transports in each of the 17 levels (Table 1).

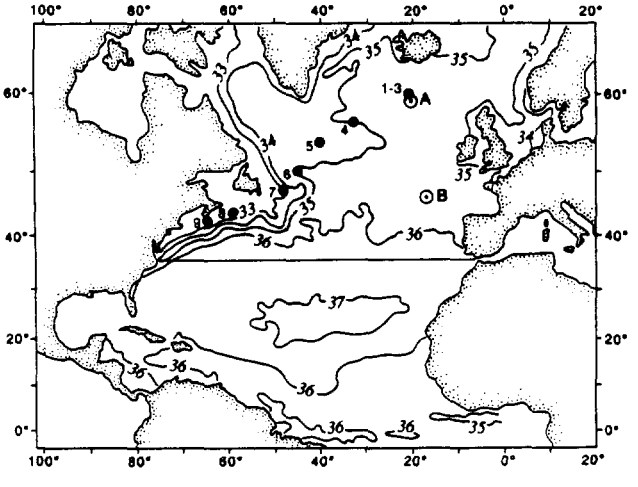

Fig. 1. The distribution of salinity in the North Atlantic at a depth of 30 m (after *Worthington* [1976]) in relation to (1) a trans-Atlantic hydrographic section at 36°25'N, (2) observations of DOC_{pt} at 46°30'N (point B) and 59°30'N (point A), and (3) bio-optical estimates of Gelbstoff between Iceland and Nova Scotia (stations 1-9).

For example, as a result of heat extraction from the Gulf Stream and influx of polar water within the East Greenland Current, a precursor of North Atlantic Deep Water (NADW) is formed in the Iceland Sea [*Swift*, 1984]. South of Denmark Strait, NADW sinks to depths >4000 m and moves south as part of the Deep Western Boundary Current (DWBC) off North America [*Broecker et al.*, 1991]. This source of sinking water is a likely mechanism for the export of DOC from surface waters of the Arctic Seas [*Duursma*, 1965], providing a sequestration time scale of thousands of years.

Similarly, mixing of Labrador Current Water (LCW) with the western boundary current to the east of the Grand Banks (note the packed isopleths of salinity in Figure 1) results in about 4 Sv of water cabelling to depths >2000 m [*Krauss et al.*, 1990], the same as previously estimated for sinking surface waters of the Labrador Sea [*Sverdrup et al.*, 1942; *Wright*, 1972]. Seasonal convective overturn of additional North Atlantic Current (NAC) waters farther east in the North Atlantic basin also leads to surface mixed layer depths of >400 m [*Levitus*, 1982] in the northeast end of the subtropical gyre, where Ekman pumping and lateral induction [*Pedlosky*, 1990; *Huang*, 1990] may further sequester DOC. Finally, some of the southward flow from the Greenland, Iceland, and Labrador Seas exits the Middle Atlantic Bight (MAB) at Cape Hatteras [*Chapman and Beardsley*, 1989], where the shelf water is subducted to depths >100 m along the northwest wall of the Gulf Stream [*Lillibridge et al.*, 1990].

The Arctic Ocean is analogous to the head of a large North Atlantic estuary [*Walsh et al.*, 1989], where 74% of the freshwater discharge (Figure 1) and associated terrestrial DOC loading of the northern hemisphere occur [*Walsh*, 1988]. A significant part of the total sequestration of DOC released within coastal, slope, and basin ecosystems may thus take place along the northwestern edges of the Gulf Stream System in the North Atlantic. This could occur within sinking surface waters via NADW formation, LCW cabelling, basin convective mixing, and shelf water subduction, part of which may flow south across 36°25'N at respective depths of perhaps 3400-4300 m, of 1600-3100 m, of 600-750 m, and of 100-350 m (Table 1).

At other depths, currents flow north, of course, such that the net exchange of water across 36°25'N is negligible (Table 1). Is the net exchange of DOM also zero? In an attempt to answer this question, we estimate the possible stocks of both DOC_{pt} and DOC_{uv} at each depth interval along 36°25'N.

To place the southward transfer of DOM within sinking water of different origins in the context of its surface supply, we also estimate the possible excretory release of DOM by various groups of plankton, as a function of particulate primary production of each shelf, slope, and basin region [*Platt et al.*, 1991]. An implicit assumption of this analysis is that oxidation of the excreted DOM within sinking waters takes place at depth, such

TABLE 1. The Estimated Meridional Fluxes of DOC_{pt} and DOC_{uv} Across 36°25'N in the North Atlantic

Depth Layer, m	Transport, Sv	Water Type	$DOC_{pt}(DOC_{uv})$ Stock, g m^{-3}		$DOC_{pt}(DOC_{uv})$ Flux, x 10^3 kg s^{-1}	
0-100	15.2	GS	2.83	(0.80)	43.02	(12.16)
100-350	-1.5	shelf	[20.00	(10.80),	[-30.00	(-16.20),
			11.32	(6.12),	-16.98	(-9.18),
			2.83	(1.53)]	-4.25	(-2.30)]
350-600	2.2	GS	2.83	(0.80)	6.23	(1.76)
600-750	-4.1	NAC	1.50	(0.42)	-6.15	(-1.72)
750-900	2.4	GS	1.20	(0.34)	2.88	(0.82)
900-1200	3.1	AIW	0.90*	(0.25)	2.79	(0.78)
1200-1400	1.6	GS	1.20	(0.34)	1.92	(0.54)
1400-1800	-2.1	LCW/GS	2.10	(0.59)	-4.41	(-1.24)
1800-2100	-3.3	LCW	3.00	(0.85)	-9.90	(-2.81)
2100-2400	-1.4	LCW	3.00	(0.85)	-4.20	(-1.19)
2400-2800	-0.5	LCW	3.00	(0.85)	-1.50	(-0.43)
2800-3100	-0.2	LCW	3.00	(0.85)	-0.60	(-0.17)
3100-3400	1.1	ACPW	1.25	(0.35)	1.38	(0.39)
3400-3700	-0.1	NADW	1.65	(0.47)	-0.17	(-0.05)
3700-4000	-5.3	NADW	1.65	(0.47)	-8.75	(-2.49)
4000-4300	-6.6	NADW	1.35	(0.38)	-8.91	(-2.51)
4300-4600	-0.4	AABW	1.25	(0.35)	-0.50	(-0.14)
Total	+0.1				[-16.87	(-12.50),
					-3.85	(-5.48),
					+8.88	(+1.40)]

The layer transports (Sv) are from *Rintoul* [1988] and the $DOC_{pt,uv}$ concentrations are from *Bauer* [1991] and the text. The water types are subducting shelf water within the Gulf Stream (GS), convecting North Atlantic Current (NAC) water, cabelling Labrador Current Water (LCW), and sinking North Atlantic Deep Water (NADW), Antarctic Intermediate Water (AIW), Antarctic Circumpolar Water (ACPW), and Antarctic Bottom Water (AABW). A negative sign denotes southward transport of water and $DOC_{pt,uv}$.

*From *Bauer* [1991].

that losses of photo-oxidation and bacterial degradation in the euphotic zone are ignored.

3. Results

3.1. *Shelf Waters*

We first use aircraft and ship bio-optical data to infer possible DOC stocks near Cape Hatteras (Figure 2), where perhaps 72% of the particulate organic carbon (POC) flux of the Gulf Stream is derived from the adjacent South and Middle Atlantic shelves [*Walsh*, 1992]. In contrast, the disparity in half-lives of the long-lived DOC and the short-lived POC pools [*Legendre and Gosselin*, 1989] should lead to much longer residence for DOC, such that some of the DOM off Cape Hatteras may have a multiyear origin, both from waters within the East Greenland Current [*Chapman and Beardsley*, 1989] and the Mississippi River plume [*Atkinson and Wallace*, 1975]. This situation would, of course, violate spatial assumptions of linear covariation of DOC, chlorophyll, and phaeopigments, needed for accurate satellite algorithms within coastal and perhaps oceanic waters [*Gordon and Morel*, 1983].

Using Coastal Zone Color Scanner (CZCS) imagery, for example, the mean primary production of North Atlantic shelf waters, between 11°-70°N (Table 2), is estimated to be 732 g C m^{-2} yr^{-1} [*Platt et al.*, 1991], with the assumption that the upwelling radiances, sampled by the satellite radiometer, represent mainly chlorophyll. This is not always true, of course, particularly in Case 2 coastal waters [*Morel and Prieur*, 1977], where humic matter

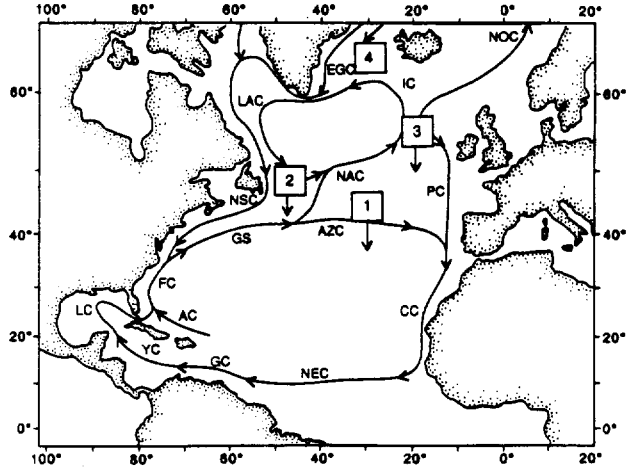

Fig. 2. A prospectus for DOM sequestration within sinking waters of the North Atlantic during subduction of shelf water (area 1), cabelling of slope water (area 2), convective overturn and lateral induction of basin water within NAC (area 3), and formation of NADW (area 4).

TABLE 2. Mean Carbon Fixation (g C m^{-2} yr^{-1}), Total Photosynthesis (x 10^{15} g C yr^{-1}), Terrestrial Input (x 10^{15} g $DOC_{pt,uv}$ yr^{-1}), Marine Excretion (x 10^{15} g DOC yr^{-1}), and NAC Contribution to NADW (x 10^{15} g $DOC_{pt,uv}$ yr^{-1}) With Respect to Sinking Waters Within Shelf, Slope, and Basin Areas (x 10^{6} km^2) of the North Atlantic Ocean

Sinking Water	Origin	Latitude	Mean C Fixation	Area	Total Production	Excretion/ Advection
GS	shelf	11°-70°N	732[366]	2.5	1.83[0.92]	0.37[0.19]
	land	11°-70°N	-	-	0.35 Sv x 12(6.5) g m^{-3}	0.13(0.07)
LCW	slope	38°-70°N	329	3.4	1.12	0.22
	basin	38°-50°N	319	3.1	0.99	0.20
NAC	basin	51°-70°N	185	5.4	1.00	0.20
NADW	shelf	71°-80°N	150	0.7	0.11	0.02
	basin	71°-80°N	150	0.5	0.08	0.02
	NAC	71°-80°N	-	-	2.00 Sv x 3(0.85)g m^{-3}	0.19(0.05)

prevails [*Carder et al.*, 1989]. The Gelbstoff, or colored dissolved organic carbon (CDOC), absorption coefficient on the Alabama-Florida shelves, for example, is as large as 0.054 m^{-1} [*Carder et al.*, 1989], and is equivalent in absorption to a chlorophyll concentration of 1 mg chl m^{-3}.

More traditional ^{14}C estimates of carbon fixation on North Atlantic shelves, between 11°-70°N, instead suggest a mean annual production of 159 g C m^{-2} yr^{-1} [*Walsh*, 1988]. We will evaluate these different estimates of primary production, and associated DOC release, after estimation of the stocks and sinking fluxes of DOM of different shelf origins. If DOC is a major factor in the contamination of color signals detected by passive satellite and active aircraft remote sensors [*Walsh*, 1988], what are the implications for regional carbon budgets?

3.1.1. *DOC stocks.* Away from coastal regions, where terrestrial DOM signals are the strongest, the abundance of marine Gelbstoff, and therefore light absorption, generally increases with the amount of annual primary production [*Carder et al.*, 1989]. Within the Sargasso Sea during December 1984, an unproductive time of year [*Menzel and Ryther*, 1960], for example, the ratio of the diffuse attenuation coefficients, k_d, for Gelbstoff or CDOC, and k_p, for the particulate matter (chlorophyll and its degradation products), at 441 nm ranged from 0.3 to 0.7, depending on the optical model [*Topliss et al.*, 1989]. This range is consistent with a mean value of 0.6 at 440 nm for the respective absorption coefficients, a_d/a_p, in the Gulf of Mexico [*Carder et al.*, 1989], since $a \approx k \cdot \cos \theta$, where θ is the subsurface solar zenith angle.

At December shelf and slope stations in the MAB, k_d/k_p was instead a mean of 2.1 [*Topliss et al.*, 1989], with ratios ranging as high as 3.6, the value of a_d/a_p observed after bloom senescence in coastal waters of the Gulf of Mexico [*Carder et al.*, 1989]. High values of this ratio imply excess amounts of colored dissolved organic matter (CDOM) on the continental margins, compared to steady state conditions. This situation results from an unknown time integral of both terrestrial influxes of CDOC and marine CDOC byproducts of previous local shelf primary production.

The winter *Topliss et al.* [1989] data can be converted to estimates of $DOC_{pt,uv}$ by first estimating the amount of CDOC. Using mass-specific absorption coefficients for marine humic and fulvic acids [*Carder et al.*, 1989], an average cosine of $\cos \theta \approx 0.82$, the spectral slope of 0.013 nm^{-1} for the winter *Topliss et al.* [1989] data, and a CDOC mixture of 16% humic and 84% fulvic acids [*Carder et al.*, 1989], we compute the entries of Table 3 from

$$a_d(\lambda) = a_d(450)\ e^{[0.013\ (450-\lambda)]} \qquad (1)$$

where $a_d(450) = 0.031$ CDOM, and CDOM = 2 CDOC. We obtain means of 2.2 and 0.17 g CDOC m^{-3} due to marine humus within respective shelf/slope and basin waters (Table 3).

Is such a 10-fold winter gradient of CDOC between shelf and basin waters representative of all seasons, and does it reflect similar gradients of total DOC? The previous wet oxidation techniques, which yield full recovery of humic and fulvic acids (all of our computed CDOC in Table 3), suggest that CDOC constitutes 20-50% of the total DOC_{uv} [*Harvey et al.*, 1983], with a C/N ratio of 34 [*Meyers-Schulte and Hedges*, 1986]. However, humic matter, measured by the platinum method, may account for only 6-14% and 11-27% of the total DOC_{pt}, since *Suzuki and Tanoue* [1991] indicate that DOC_{pt} may be 3.54 x DOC_{uv} in unproductive areas and 1.85 x DOC_{uv} in rich regions.

As much as 33% of the DOC_{pt} may instead be reactive polysaccharides [*Benner et al.*, 1992]. Furthermore, the photo-chemical production of low molecular-weight organic compounds from humic substances in natural waters [*Keiber et al.*, 1989, 1990] suggests that the ratio of humic (H) and fulvic (F) acids to total DOC decreases with time in surface waters, given no other sources or sinks. This process is perhaps discernable within *Harvey et al.*'s [1983] observations for depths ≤ 20 m in the Gulf of Mexico, during fertile (spring) and unproductive (fall) periods of the year.

Except for one measurement during a senescent bloom off Cape San Blas, their spring data [*Harvey*

TABLE 3. Mean Pigment Concentrations (mg m^{-3}), Absorption Coefficients (m^{-1}), and Colored Dissolved Organic Carbon (g m^{-3}) Within MAB Shelf/Slope and Sargasso Sea Waters

	Chl a	Phaeo a	$a_p(441)$	$a_d(441)$	CDOC	DOC_{pt}
MAB shelf/ slope	1.84	0.59	0.072	0.153	2.20	20.00
Sargasso Sea	0.35	0.22	0.025	0.012	0.17	2.83

These values are based on both *Topliss et al.* [1989] measurements and models, and on mass-specific absorption coefficients for a mixture of 15% humic and 85% fulvic acids [*Carder et al.*, 1989], consistent with a spectral slope, S_λ, of 0.013 nm^{-1} for the absorption by colored dissolved organic matter (CDOM) in December 1984. Diffuse attenuation coefficients were converted to absorption coefficients by a = 0.82 k, while CDOC/CDOM = 0.5, and DOC_{pt} is computed from 1.85 DOC_{uv} in coastal waters and from 3.54 DOC_{uv} in oceanic waters.

et al., 1983] can be expressed by the regression

$$DOC_{uv} = 0.30 + 0.78(H+F), \quad (2)$$

whereas the fall data fall along a line expressed by

$$DOC_{uv} = 0.90 + 0.43(H+F) \quad (3)$$

The intercept value of (3) for fall conditions, i.e., the portion of DOC_{uv} which does not covary with (H+F), is threefold that of (2) for spring waters. Such a trend may reflect photolysis of some of the light-absorbing (H+F), which would be reflected in a smaller CDOC/DOC ratio.

Accordingly, we compute the offshore stock of 2.83 g DOC_{pt} m^{-3} (Table 3) in the Gulf Stream with a $CDOC/DOC_{pt}$ ratio of 0.06, and the shelf stock of 20 g DOC_{pt} m^{-3} with a ratio of 0.11. We employ these smaller ratios to emphasize both photolysis of CDOC and the other labile fractions of DOM, captured with the platinum method, since our $CDOC/DOC_{uv}$ ratio is 0.20, when DOC_{pt} = 1.85 DOC_{uv} in coastal waters, and 0.21, when DOC_{pt} = 3.54 DOC_{uv} in oceanic waters [*Suzuki and Tanoue*, 1991]. Except for the shelf estimates of Table 1, all other values of DOC_{uv} at different depths assume oceanic DOC_{pt} = 3.54 DOC_{uv}.

Our estimated DOC_{pt} stock for offshore surface waters (Table 1) approximates the previous dry combustion measurements of about 3.6 g DOC m^{-3} at the edge of the Nova Scotian shelf and 2.4 g DOC m^{-3} in the Sargasso Sea [*Gordon and Sutcliffe*, 1973]. How realistic is the nearshore estimate of DOC_{pt} stocks (Table 3), however? Riverine concentrations of as much as 42.6 g DOC_{pt} m^{-3} (1.85 x prior DOC_{uv} of *Wei-Bin et al.* [1983]) evidently suffer rapid dilution on the adjacent shelf of the East China Sea, with only 5.8 g DOC_{pt} m^{-3} found at mid-shelf in the Yangtze River plume and 3.1 g DOC_{pt} m^{-3} in the Kuroshio [*Suzuki and Tanoue*, 1991]. We thus consider a range of three $DOC_{pt,uv}$ stocks for shelf waters in Table 1 and compute their offshore fluxes within sinking water, for comparison with the total inputs of DOC from land and from release by the marine food web (Table 2).

3.1.2. *Sinking water.* Containing a distinct diatom assemblage of nearshore species, the shelf water at Cape Hatteras is subducted to depths >100 m underneath the western boundary current [*Lillibridge et al.*, 1990]. Along a downstream distance of 150 km, for example, the subsurface core of low salinity water (and associated DOC stock) descended from a depth of ~75 m at 50 km seaward of the Cape Hatteras shelf-break to ~125 m during an October 1985 study of the Gulf Stream. Eastward transfer within the downstream North Atlantic and Azore Currents over months to years will smear such land/shelf DOC signals, of course, like that of radium 228 [*Sarmiento et al.*, 1990].

We estimate the possible sinking loss, however, by assuming a surface width of low-salinity waters of shelf origin to be perhaps 15 km along the northwest wall of the Gulf Stream at 37°N. Over a depth interval of at least 100 m at a speed of 1 m s^{-1}, the transport within the first 15 km of the nearshore Gulf Stream would be 1.5 Sv of water. This transport is similar to that of 1 Sv estimated for the combined water fluxes from the South and Middle Atlantic shelves at the 100-m isobath off Cape Hatteras [*Walsh*, 1992].

If subduction were to occur all year, continued storage of a combination of terrestrial and shelf DOC, like radium 228 and O_2 [*Sarmiento et al.*, 1982, 1990], may occur within the main pycnocline of the subtropical gyre of the North Atlantic. Here, arguments about local oxygen utilization and primary production rates off Bermuda [*Jenkins and Goldman*, 1985; *Platt and Harrison*, 1986] may be confounded by these lateral supplies of organic matter, albeit DOC rather than non-sinking POC [*Martin et al.*, 1987]. Depending upon transit time and subsurface respiration losses, the southward dispersion of the shelf DOC signals may be a seasonal, or a multiyear, process.

To employ a suitable averaging scheme across these time scales, we construct a zonal mean of the possible meridional transport, over 17 depth intervals, of $DOC_{pt,uv}$ across 36°25'N latitude. A southward transport in Table 1 of 1.5 Sv of water over a depth interval of approximately 100-350 m (a density interval of 26.4 to 26.8 σ from *Roemmich and Wunsch* [1985]) is obtained by averaging over the 6000-km length of this section (Figure 1). Such a southward transport of water and oxygen at this depth interval [*Rintoul*, 1988] is assumed by

us to also represent the fate of shelf and land DOC, subducted at the surface (Figure 2) along ~40°N between 20°-70°W [*Huang*, 1990], with possible equatorward transfers of 4.25 to 30 x 10^3 kg DOC_{pt} s^{-1} into the upper pycnocline of the subtropical gyre (Table 1).

Although the vertical structure of the ^{14}C age of DOC_{pt} in the water column off Bermuda has not yet been sampled with the same resolution as Table 1, early results [*Bauer*, 1991] confirm our assumptions of a recent source of DOC within the upper pycnocline. At a depth of about 500 m, a subsurface minimum in the radiocarbon age of DOC_{pt} was observed (about -275‰), indicating a relatively young origin. In contrast, a $\Delta^{14}C$ value of -450‰ was measured for a DOC stock of 0.9 g DOC_{pt} m^{-3} (Table 1) within the oxygen minimum layer near a depth of 850 m [*Bauer*, 1991].

3.1.3. *Excretory supply*. If we first assume the combined land and shelf DOC stock to be 20 g DOC_{pt} m^{-3}, the southward DOC flux along the northwest wall of the Gulf Stream might be as high as 30 x 10^3 kg DOC_{pt} s^{-1} (Table 1), or 0.9 x 10^{15} g DOC_{pt} yr^{-1} on an annual basis. This is presumably an upper bound, since it is almost twice the larger estimate of land and shelf supply of DOC to the North Atlantic shelves (Table 2). A smaller DOC_{uv} shelf stock of 10.8 g m^{-3} and the same water transport of 1.5 Sv yield instead an export of 16.2 x 10^3 kg DOC_{uv} s^{-1} (Table 1), or 0.5 x 10^{15} g DOC_{uv} yr^{-1}; this is still larger than the estimated inputs of terrestrial and marine DOC_{uv}.

A very large total primary production of 1.83 x 10^{15} g C yr^{-1} over a shelf area of 2.5 x 10^6 km^2 [*Platt et al.*, 1991], for example, and a phytoplankton excretion rate of 20% of this carbon fixation yield a marine excretory input of 0.37 x 10^{15} g DOC yr^{-1} (Table 2). A total freshwater discharge of 1.1 x 10^{13} m^3 yr^{-1} to the North Atlantic shelves between 11°-70°N [*Walsh*, 1988] and a mean terrestrial DOC concentration of 12 g DOC_{pt} m^{-3} (1.85 x 6.5 g DOC_{uv} m^{-3} of *Spitzy et al.* [1991]) suggest a possible land input of either 0.7 x 10^{15} g DOC_{uv} yr^{-1}, or 1.3 x 10^{15} g DOC_{pt} yr^{-1}. If these estimates of photosynthesis, excretion, and terrestrial supplies of DOC are all correct, the combined sources sum to 0.44 x 10^{15} g DOC_{uv} yr^{-1} and 0.50 x 10^{15} g DOC_{pt} yr^{-1} (Table 2).

Mean excretion rates of shelf phytoplankton range from 5% (n=21) of primary production in the South Atlantic [*Thomas*, 1971], 17% (n=838) in the Middle Atlantic [*Thomas et al.*, 1979], to 38% (n=4) in the North Atlantic [*Choi*, 1972] Bights, suggesting an average of 20%. Such a shelf DOC release rate is similar to respective means of 22-23% for phytoplankton excretion of DOC in slope (n=4) and basin (n=5) regions of the western North Atlantic [*Thomas*, 1971; *Choi*, 1972]. When these data are pooled with the results of 14 other regional studies [*Sharp*, 1977], a grand mean excretion rate of 23% is obtained.

Sharp [1977] suggested that the high excretion rates of phytoplankton might be experimental artifacts, but analysis of more recent data suggests a mean rate of 13%, which meets less than half of the substrate demands of coexisting bacterial populations [*Baines and Pace*, 1991]. Thus far, we have ignored releases of DOC by zooplankton [*Jumars et al.*, 1989] and bacterioplankton [*Brophy and Carlson*, 1989], thereby underestimating the biotic supply of DOC. An excretory release rate of 20% approximates the numerous observations of phytoplankton excretion in the MAB [*Thomas et al.*, 1979] and allows for some heterotrophic input of DOC as well [*Baines and Pace*, 1991].

We believe that the satellite estimate of a shelf primary production of 732 g C m^{-2} yr^{-1} [*Platt et al.*, 1991] may be too large, however, because of coastal stocks of DOC, sensed as chlorophyll biomass by the CZCS. If the remotely sampled DOC concentrations constitute half of the color signal of coastal waters [*Hochman*, 1992], and the specific photosynthetic rate (yr^{-1}) remains the same, the actual primary production might be 366 g C m^{-2} yr^{-1} (Table 2). A smaller excretory input of 0.19 x 10^{15} g DOC yr^{-1} would follow (Table 2), supporting less of a shelf export of DOC to be subducted beneath the Gulf Stream. We thus consider the case of an intermediate seaward DOC flux, estimated by aircraft sensors, and then a third scenario of no difference between shelf and basin stocks of DOC.

Active remote sensors on aircraft [*Hoge and Swift*, 1981] sample at 10^3 faster rates than shipboard surveys [*Walsh et al.*, 1988], such that the laser-induced measurement of a fourfold range in Gelbstoff concentrations, between coastal and offshore waters in December [*Topliss et al.*, 1989], may be more accurate than the spatial assessment of DOC abundance from a few ship stations. Accordingly, we estimate that the shelf stock of DOM might instead be an intermediate 11.32 g DOC_{pt} m^{-3}, fourfold the basin concentration (Table 1). In this case, the offshore fluxes of DOM would be 17 x 10^3 kg DOC_{pt} s^{-1} and 9.2 x 10^3 kg DOC_{uv} s^{-1} (Table 1). Over a year, these possible sinking fluxes of 0.3 x 10^{15} g DOC_{uv} yr^{-1} -0.5 x 10^{15} g DOC_{pt} yr^{-1} represent all of the combined terrestrial and shelf supplies of 0.26-0.32 x 10^{15} g DOC yr^{-1} (Table 2).

Finally, the no-DOC-gradient scenario yields offshore fluxes of 2.3 x 10^3 kg DOC_{uv} s^{-1} and 4.2 x 10^3 kg DOC_{pt} s^{-1} (Table 1), or 0.07-0.13 x 10^{15} g DOC yr^{-1}, i.e., only 27-41% of the coastal supplies of DOC at a reduced annual rate of photosynthesis of 366 g C m^{-2} yr^{-1} (Table 2). The offshore decline of primary production, from 732 [366] to 329 g C m^{-2} yr^{-1} (Table 2), may reflect less contamination by DOC of the satellite estimates of chlorophyll biomass in slope regions. Within basin regions between 38°-50°N and 51°-70°N, the respective rate of photosynthesis is even smaller, from 319 to 185 g C m^{-2} yr^{-1} (Table 2); we thus assume that the estimates of primary production in slope and basin waters [*Platt et al.*, 1991] are correct for the purposes of our carbon budgets.

3.2. *Slope Waters*

3.2.1. *DOC stocks*. We next consider how much surface DOC stocks might be cabelled downward as a mixture of the Labrador and North Atlantic Currents to depths of 1400-2400 m on the Newfoundland slope [*Krauss et al.*, 1990]. Of the 90-100 Sv transport of the Gulf Stream at 70°W [*Johns et al.*, 1989] and 55°W [*Richardson*, 1985], part recirculates to the west, part moves southeast as the Azores Current (Figure 2), and about 33 Sv proceeds northeastward as the NAC [*Krauss et al.*, 1990].

With movement towards the northeast at 0.5-1.0 m s^{-1}, between the subarctic and subtropical gyres of the North Atlantic [*Smith et al.*, 1990], this downstream western boundary current, east of the Grand Banks, should still have a Gulf Stream DOC content of 2.83 g DOC_{pt} m^{-3} (Table 1), assuming a half-life for the labile DOC of about 25-50 years

[*Keiber et al.*, 1990; *Toggweiler*, 1990; *Bacastow and Maier-Reimer*, 1991]. We then need an estimate of the DOC content of the coastal end member of this mixing pair.

The actual source regions of shelf DOC entrained at Cape Hatteras may extend from north of Greenland [*Chapman and Beardsley*, 1989] to at least the Mississippi River [*Atkinson and Wallace*, 1975] as a result of longshore coherence of flow and the long half-life of some DOC components. In contrast to the Mississippi and Hudson Rivers, where urban DOC fluxes constitute as much as 90% of the daily carbon loading of 8-10 g DOC_{uv} m^{-3} [*Mueller et al.*, 1976; *Segar and Berberian*, 1976; *Thomas et al.*, 1979; *Leenheer*, 1982], the DOC content of the relatively pristine St. Lawrence River is now less than half, about 2-4 g DOC_{uv} m^{-3} [*Pocklington and Tan*, 1983]. We might thus expect the additional DOC loading of the western North Atlantic from subarctic shelf waters (Figure 2), partially derived from pristine Arctic Rivers, to be less than at mid-latitudes.

Accordingly, we assume that the 2 Sv of shelf water, draining the Canadian Archipelago via Davis Strait [*Chapman and Beardsley*, 1989; *Walsh et al.*, 1989] contains 6 g DOC_{pt} m^{-3} (1.85 x 3.24 g DOC_{uv} m^{-3} [*Pocklington and Tan*, 1983]). A mixture of 2 Sv of this shelf water, with 6 g DOC_{pt} m^{-3}, and 33 Sv of prior Gulf Stream water, with 2.83 g DOC_{pt} m^{-3}, yields a recirculating NAC transport (Figure 2) of 35 Sv, containing 3 g DOC_{pt} m^{-3} (Table 1). Part of this augmented NAC sinks in the Labrador Sea as cabelled slope water, and part sinks in the eastern Atlantic as convected basin water (Figure 2).

3.2.2. *Sinking water.* At least 4 Sv of water cabells along the Newfoundland slope to join the DWBC at depths >2400 m [*Krauss et al.*, 1990]. This estimate is similar to prior transport calculations of sinking surface water in this region [*Sverdrup et al.*, 1942; *Wright*, 1972]. Over a year, continuous sinking of this amount of water would yield an annual slope DOC sequestration of 0.1 x 10^{15} g DOC_{uv} yr^{-1} to 0.4 x 10^{15} g DOC_{pt} yr^{-1}, i.e., half, or double, the estimated excretory supply of DOC within just slope regions over 38°-70°N (Table 2).

3.2.3. *Excretory supply.* Over the northern slope area of 3.4 x 10^6 km^2, a total photosynthesis of 1.12 x 10^{15} g C yr^{-1} [*Platt et al.*, 1991] and a 20% excretion rate yield an excretory release of 0.22 x 10^{15} g C yr^{-1} within the nearshore mixing member (Table 2). Over a similar basin area of 3.1 x 10^6 km^2, between 38°-50°N, more primary production of 0.99 x 10^{15} g C yr^{-1} yields another excretory input of 0.20 x 10^{15} g C yr^{-1} (Table 2). Their sum balances the advective loss of DOC_{pt} within 4 Sv of sinking Labrador Current Water (LCW).

If the DOC_{pt} measurements are artifacts, however, as a result of organic contaminants of the catalysts or poor blanks, for example, less biotic supply of DOC is required to balance sinking losses of DOC_{uv} within LCW. The sequestration of 0.1 x 10^{15} g DOC_{uv} yr^{-1} within 4 Sv of LCW only requires the supply of dissolved photosynthate over a smaller area of ~1.6 x 10^6 km^2, i.e., along the Labrador slope between 50°-60°N. On the other hand, if all of the southward transport of 6.8 Sv of LCW across 36°25'N (Table 1) represents just one year of ventilation of surface waters, and the DOC_{pt} stocks are not artifacts, the associated equatorward flux of DOC would be 0.6 x 10^{15} g DOC_{pt} yr^{-1}, i.e., 150% of the sum of slope and basin supplies of DOC (Table 2).

3.2.4. *Southern Ocean supply.* In terms of a meridional flux of DOC across 36°25'N, we thus assume that 5.4 Sv of LCW, over a depth range of 1800-3100 m, represents a recent influx from the Labrador Sea. The relict DOC stocks at 1400-1800 m are instead assumed to be a mixture of LCW and Gulf Stream waters, in which the lower values of DOC represent respiration losses of multiyear inputs from Antarctic source regions; specifically within Antarctic Intermediate Water (AIW of Table 1). Note that the DOC pools of Antarctic Circumpolar Water (ACPW) and of Antarctic Bottom Water (AABW) are estimated to be 1.25 g DOC_{pt} m^{-3} (0.35 g DOC_{uv} m^{-3}), somewhat higher than those of the oxygen minimum layer of AIW [*Bauer*, 1991].

These additional stocks of Southern Ocean origin are assumed to have initial surface values of 1.5 g DOC_{pt} m^{-3} (0.42 g DOC_{uv} m^{-3}), half that estimated for Arctic waters, to be consistent with observations of k_d in the Greenland, Barents, and Bellingshausen Seas [*Mitchell*, 1992]. Based on 302 bio-optical measurements in these Seas, the diffuse attenuation coefficient due to dissolved substances, k_d, at 441 nm is 0.036 m^{-1} in the Antarctic, compared to 0.063 m^{-1} in the Arctic. This situation may result from greater terrestrial loading [*Mitchell*, 1992], and/or larger marine photosynthetic [*Walsh*, 1989] release, of DOC in the Arctic.

3.3. *Basin Waters*

To explore the basin (>2000 m) sinking losses of DOC, we estimate how much might be sequestered in the North Atlantic by two convective processes: (1) overturn and lateral induction of NAC waters into the subtropical gyre, south of 50°N [*Huang*, 1990], and (2) overflow of NADW [*Swift*, 1984] across the 600-m sill of Denmark Strait at 65°N.

3.3.1. *NAC transfers.* Before transformations of the NAC into the Irminger, Norwegian, and Portugal Currents (Figure 2), seasonal convection occurs en route in the northern North Atlantic, with deepening of the surface mixed layer [*Levitus*, 1982]. North of 50°N, for example, where the depth of the surface mixed layer in February can exceed 700 m [*McClain et al.*, 1990], convective overturn of part of the NAC may result in lateral induction of an equatorward transport of at least 4.1 Sv, which could reach a depth interval of 600-750 m across 36°25'N (Table 1).

With a NAC stock of 3 g DOC_{pt} m^{-3}, this transfer would amount to a southward flux of 12.3 x 10^3 kg DOC_{pt} s^{-1}, or 0.4 x 10^{15} g DOC_{pt} yr^{-1} over 12 months. If this shallow portion of the basin export of DOC from the northern North Atlantic does occur year round, it represents twice the estimated annual release of DOC within surface waters between 51°-70°N (Table 2).

A small carbon fixation of 185 g C m^{-2} yr^{-1} over 5.4 x 10^6 km^2 and a 20% excretion rate yield a release of 0.2 x 10^{15} g DOC yr^{-1} (Table 2). Such low rates of photosynthesis [*Thomas*, 1971] may lead to larger percentages of DOC excretion by oceanic microflagellates [*Wolter*, 1982], perhaps even during spring blooms of this region [*Kirchman et al.*, 1991]. A larger excretion rate of 40%, for example, would allow a biotic influx of 0.4 x 10^{15} g DOC yr^{-1}.

An alternative hypothesis is a seasonal decline of photosynthesis and of DOC release during light-limited periods of the year, when initiation of the southward transfer of overturned NAC occurs. The

mean depth of the surface mixed layer at 59°30'N, 20°30'W deepens, for example, from 45.1 m during May-October to 432.2 m during November-April (based on the $\Delta T/\Delta z$ criterion of 0.5°C [*Levitus*, 1982]). Finally, a third scenario would be to discard the DOC_{pt} estimate of NAC stocks in favor of an annual southward NAC flux of 0.11 x 10^{15} g DOC_{uv} yr^{-1}.

Since *Duursma* [1965] suggested that there might be a seasonal influx of surface Arctic DOC stocks to deep waters via sinking NADW as well, we implement the second hypothesis in Table 1. We represent this process by a 50% reduction of the NAC stock to 1.5 g DOC_{pt} m^{-3} (Table 1) to reflect lower winter values, yielding an annual export across 36°25'N of 0.2 x 10^{15} g DOC_{pt} yr^{-1}. Validation of this hypothesis of seasonal DOC release is seen in the higher summer values of DOC_{pt} within surface waters between 47°-59°N (Figure 3). A similar logic is invoked for DOC export within sinking NADW.

3.3.2. *NADW transfers*. A continuous tongue of relatively high DOC, about 0.7 g DOC m^{-3} with early techniques [*Duursma*, 1965], could be traced from surface to bottom waters south of Iceland, within NADW during April 1958, but not in the following September. More recent data suggest intermediate values of 0.8-1.2 g DOC_{uv} m^{-3} at the surface of the Lincoln Sea [*Gordon and Cranford*, 1985], compared to prior observations of 2-3 g DOC m^{-3} in the Canadian Basin [*Melnikov and Pavlov*, 1978]. Assuming a 3.54 underestimate of DOC_{uv} in these unproductive regions (Table 2) yields a possible mean stock of 3.5 g DOC_{pt} m^{-3} within Arctic precursors of NADW in the Greenland and Iceland Seas.

If we further assume that all 5 Sv of the transport of the East Greenland Current (3 Sv of polar origin, 2 Sv of Atlantic origin [*Aagaard and Reed*, 1987]) are converted to NADW above Denmark Strait, we obtain the same estimate for NADW formation as *Worthington's* [1976] calculation: 4 Sv through Denmark Strait and 1 Sv across the Iceland-Scotland ridge. Such a mixture of the NAC and the East Greenland Current end members yields a possible DOC stock for NADW of 3.3 g DOC_{pt} m^{-3} (0.9 g DOC_{uv} m^{-3}). Over 12 months, the NADW export of DOC from the Iceland and Greenland Seas might then be either 0.15 x 10^{15} g DOC_{uv} yr^{-1}, or 0.52 x 10^{15} g DOC_{pt} yr^{-1}, i.e., ignoring seasonality in the release and sequestration of DOC.

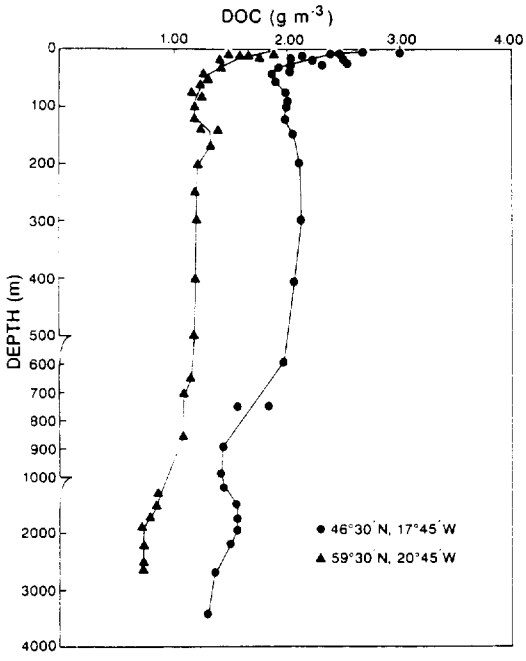

Fig. 3. The vertical structure of DOC_{pt}, as measured by Y. Suzuki, during May-June 1989 in temperate and subarctic regions of the eastern North Atlantic (see Figure 1 for the locations of these regions).

Once more, this estimate is an upper bound, because a mean carbon fixation of 150 g C m^{-2} yr^{-1} [*Eilertsen et al.*, 1989], over both the 0.7 x 10^6 km^2 shelf of the Barents Sea [*Walsh*, 1988] and the 0.5 x 10^6 km^2 basin of the Greenland Sea [*Carmack and Aagaard*, 1973], only sums to 0.19 x 10^{15} g C yr^{-1} (Table 2). An excretion rate of 20% then provides a combined shelf/basin influx of at most 0.04 x 10^{15} g DOC yr^{-1} within local waters. The supply of 2 Sv of NAC from the south, with a stock of 3 g DOC_{pt} m^{-3}, may contribute 0.19 x 10^{15} g DOC_{pt} yr^{-1} to NADW (Table 2).

There is presumably no net import of DOM from the Arctic Ocean via Fram Strait, however, since the same 63 mg DON m^{-3} is found [*Kattner and Becker*, 1992] under the ice in the East Greenland Current (Transpolar Drift origin) and in open waters of the West Spitsbergen Current (NAC origin), whose transport is also about 5 Sv [*Walsh et al.*, 1989]. The biogenic and advective sources of DOC within sinking NADW may thus sum to 0.09 x 10^{15} g DOC_{uv} yr^{-1}, or 0.23 x 10^{15} g DOC_{pt} yr^{-1}, i.e., half that of the above DOC exports.

By summing a constant flux over the year, we may have again overestimated the annual sequestration of DOC within sinking waters of the northern North Atlantic. Accordingly, we assume a seasonal supply of DOC within NADW (see Figure 3 for the spatial analogue), like that of NAC, with a winter estimate of 1.65 g DOC_{pt} m^{-3} (Table 1), when NADW is presumably formed. As in the case of LCW, we also assume that only 5.4 Sv of NADW transfer, over depths of 3400-4000 m along 36°25'N, represent the annual carbon loading of 0.28 x 10^{15} g DOC_{pt} yr^{-1} (Table 1).

3.3.3. *Southern Ocean transfers*. The additional 6.6 Sv of entrained NADW, over depths of 4000-4300 m, instead represent a multiyear accumulation of both Antarctic and Arctic sources, with an intermediate stock of 1.35 g DOC_{pt} m^{-3} (Table 1). Before we turn to the implications of these meridional fluxes over the whole water column at 36°25'N, we first address how realistic our estimates of the DOC stocks might be. An analysis is made of recent data taken during the 1989 and 1991 spring blooms of the North Atlantic.

4. Corroboration

4.1. *Vertical Structure*

During May 18-19 and June 5-6, 1989, Y. Suzuki measured DOC_{pt} concentrations at several stations [*Slagle and Heimerdinger*, 1991] near 59°30'N, 20°25'W and 46°30'N, 17°45'W (locations A and B of Figure 1). To provide sufficient depth resolution, we plotted his data from two adjacent stations at each location in Figure 3, which show possible signatures of cabelled slope water and overturned basin water.

The measured DOC stocks within the upper 25 m of the water column in region A (59°30'N) yield a mean (n=11) of 1.9 g DOC_{pt} m^{-3}, compared to a mean (n=10) of 2.4 g DOC_{pt} m^{-3} in region B (46°30'N), where a maximum of 3.0 g DOC_{pt} m^{-3} was found. These values at the lower latitude are equivalent to our estimates of 2.8-3.0 g DOC_{pt} m^{-3} for Gulf Stream waters and LCW along 36°25'N (Table 1). Note that the subsurface values of DOC_{pt} at the higher latitude are almost half those of surface waters, reflecting increased excretion during the spring bloom [*Kirchman et al.*, 1991].

Preservation of the vertical structure of DOC partially depends upon latitude, i.e., the extent to which local vertical mixing smears the DOC tracers introduced at the surface. Region A at 59°30'N has a sufficiently deep winter mixed layer [*Levitus*, 1982] to allow uniform stocks of 1.2 g DOC_{pt} m^{-3} over depths of 200 to 500 m (Figure 3). Fall overturn of this part of the summer water column at 59°30'N would indeed lead to a depth-averaged stock of 1.26 g DOC_{pt} m^{-3} and a mean density of 27.37 σ.

If the overturned basin waters at 59°30'N were to flow south along the 27.3-27.5 σ isopycnals after Ekman pumping [*Huang*, 1990], these DOC stocks would then occur at deeper depths of 700-900 m near both 46°30'N and 36°25'N, where we assumed a stock of 1.5 g DOC_{pt} m^{-3} for NAC (Table 1). The vertical structure of DOC at 46°30'N appears to provide similar validation of our hypothesis of LCW sequestration of excretory products.

The experimental precision of the DOC_{pt} measurements is ± 1-5%, depending upon sea state [*Slagle and Heimerdinger*, 1991], such that the 10% subsurface increment of DOC at depths of 1500-2000 m in region B, but not in region A (Figure 3), may reflect cabelling LCW. Since LCW and NADW both travel south mainly in the DWBC of the western Atlantic Ocean, as indicated by tritium dispersal and radiocarbon ages [*Broecker et al.*, 1991], we would expect their signals to be weakest in the northeastern Atlantic along 20°W. Indeed at greater depths of 2700 m in regions A and B, the respective stocks of 0.8 and 1.4 g DOC_{pt} m^{-3} are equivalent to our assumed DOC_{pt} content of ACPW and AABW (Table 1).

4.2. *Horizontal Structure*

A transect of nine stations, from site A, south of Iceland, to Nova Scotia during May-June 1991 (Figure 1), provides an assessment of the various values of shelf DOC, assumed to be subducted under the Gulf Stream at depths of 100-350 m (Table 1). The surface values of CDOM absorption at 440 nm show a linear trend with salinity, inshore of the Labrador Current (Figure 4). They are threefold higher in summer waters of the Nova Scotian shelf (Table 4), compared to either site A, or the hibernal Sargasso Sea (Table 3). The shelf observations of 0.052-0.078 m^{-1} are similar to that of 0.063 m^{-1} in the Arctic [*Mitchell*, 1992], but half the absorption values observed [*Topliss et al.*, 1989] in MAB shelf waters (Table 3).

The spectral absorption coefficients of these CDOM data were converted [*Carder et al.*, 1989] to estimates of humic and fulvic acids (Table 4). Equation (2) for a spring bloom situation of less photolysis was then used to convert (H+F) to DOC_{uv},

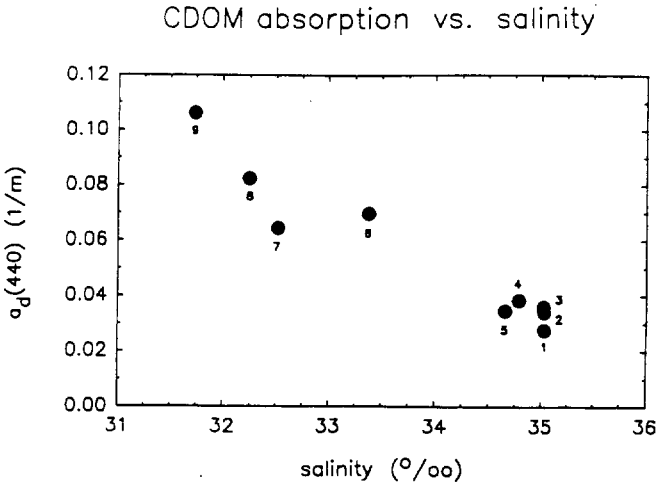

Fig. 4. The relation of Gelbstoff absorption at 440 nm to surface salinity between Iceland and Nova Scotia (see Figure 1 for locations of stations 1-9).

TABLE 4. Absorption Coefficients (a_d 440) due to DOM Within the Upper Meter at Stations of the 1991 Transect From Iceland to Nova Scotia

Station	a_d 440, m^{-1}	S_λ, nm^{-1}	H+F, g m^{-3}	DOC_{uv}, g m^{-3}	DOC_{pt}, g m^{-3}
1	0.0256	-0.0150	1.24	1.26	2.27
2	0.0344	-0.0133	1.12	1.17	2.11
3	0.0333	-0.0146	1.47	1.44	2.59
4	0.0325	-0.0150	2.05	1.89	3.40
5	0.0327	-0.0156	2.23	2.03	3.65
6	0.0603	-0.0141	2.90	2.55	4.59
7	0.0519	-0.0159	4.05	3.44	6.19
8	0.0619	-0.0160	4.84	4.05	7.29
9	0.0775	-0.0165	4.90	4.10	7.37

The samples were filtered with preflushed 0.2 μm pore diameter, Nucleopore pads, and measured in 10 cm cells of a Cary 2200 spectrophotometer. The spectral slope of the semi-log regression between 310 and 490 nm is denoted as S_λ, while the humic (H) and fulvic (F) acid concentrations are estimated from a_d 450, S_λ, and the equations provided by *Carder et al.* [1989]. Our estimates of $DOC_{uv,pt}$ are then derived from the H+F values, as discussed in the text.

yielding values of 1.16 to 1.51 g DOC_{uv} m^{-3} for stations 1-3 at site A (Table 4). With our eutrophic DOC_{pt}/DOC_{uv} ratio of 1.85, the estimated surface DOC stocks at site A in 1991 become 2.15-2.79 g DOC_{pt} m^{-3} (Table 4), compared to observations of 1.50-1.97 g DOC_{pt} m^{-3} during 1989 (Figure 3).

While these offshore observations are from different years, they are from the same site in the same season, providing a check on our hypotheses of various gradients of DOC between shelf and basin regions of the North Atlantic. Our bio-optical measurements indicate a rapid increase of DOM on the Grand Banks, with perhaps 3.5-fold greater values of DOC_{pt} on the outer Nova Scotian shelf than at site A (Table 4). Recall that the aircraft estimates of Gelbstoff fluorescence also suggested a fourfold winter gradient of DOC between coastal and oceanic waters of the MAB [*Topliss et al.*, 1989]. Furthermore, previous shipboard observations of DOM fluorescence indicate a threefold to sixfold gradient of stocks between basin waters at 60°N, 20°W and either the East Greenland Current, or shelf waters just west of Scotland [*Duursma*, 1965].

5. Conclusions

What then are the consequences of our many assumptions? We begin with the implications of the depth-integrated DOC_{pt} transports. The net DOC_{pt} transfer of the whole water column sums to a southward export across 36°25'N of 16.87 x 10^3 kg DOC_{pt} s^{-1}, or 1.4 x 10^3 kmol DOC_{pt} s^{-1}, in the case of the largest value of shelf DOC_{pt} stocks (Table 1). The same flow fields and the observed oxygen concentrations along 36°25'N yield a net southward flux of 2.9 x 10^3 kmol O_2 s^{-1} [*Rintoul*, 1988].

If we assume a molar O_2/C consumption ratio of 1.3 for bacterial degradation of subsurface carbon substrates [*Redfield et al.*, 1963], the ratio of 2.1 for the above O_2/DOC_{pt} net fluxes suggests that 63% of the AOU demands across 36°25'N would be met by sinking DOC, and 37% by falling POC, if all of the O_2 were consumed. Furthermore, a DOC/DON ratio of 10 from dry combustion [*Gordon and Sutcliffe*, 1973], which is an intermediate value between that of 5 [*Sugimura and Suzuki*, 1988] and 15 [*Benner et al.*, 1992] from platinum catalysts, suggests a net equatorward flux of 1.7 x 10^3 kg DON s^{-1}. This fortuitously balances the postulated poleward export of 1.7 x 10^3 kg NO_3 s^{-1} across 36°25'N [*Rintoul*, 1988] of unutilized nitrate within the Gulf Stream.

The smaller, fourfold gradient of DOC_{pt} between nearshore and offshore regions suggests instead a net southward flux of only 3.85 x 10^3 kg DOC_{pt} s^{-1} (Table 1), or 0.32 x 10^3 kmol DOC_{pt} s^{-1} and an O_2/DOC_{pt} ratio of 9.1. With this second scenario and the Redfield ratio, 86% of the oxidizable carbon substrate may be in particulate form, with just 14% as DOC. Using the same DOC/DON ratio, 0.4 x 10^3 kg DON s^{-1} may cross 36°25'N towards the equator, offsetting only 24% of the poleward flux of NO_3 in this case.

If we choose a larger C/N ratio, say, 15 [*Benner et al.*, 1992] or 25 [*Jackson and Williams*, 1985], then just 9-15% of the northward flux of Gulf Stream nitrate would be returned as DON in the second scenario. Larger values of shelf DOM, or greater oceanic rates of photosynthesis and excretion, would then be required to support *Rintoul and Wunsch*'s [1991] hypothesis. In contrast, a zero seaward gradient of DOC_{pt} leads to a net poleward transfer of 8.88 x 10^3 kg DOC_{pt} s^{-1} in the third case (Table 1), such that no DON would move equatorward.

Even if the DOC_{pt} estimates are artifacts, the net DOC_{uv} fluxes show a similar pattern (Table 1). Because of the different DOC_{pt}/DOC_{uv} ratios used for shelf and oceanic waters (1.85 versus 3.54), the second DOC_{uv} scenario reflects an eightfold gradient of DOC_{uv}, while the third case poses a twofold gradient. In this third scenario, no DOC_{uv}, nor DON, are exported south from the northern North Atlantic (Table 1).

In contrast, the second case yields a net southward export of 5.48 x 10^3 kg DOC_{uv} s^{-1} (Table 1), with an O_2/DOC_{uv} ratio of 6.3. This calculation suggests that 79% of the AOU demands might be met by POC, and 21% by DOC_{uv}, similar to *Ogura*'s [1970] conclusions. Only 32% of the proposed northward influx of NO_3 would then be returned south as DON, leaving open the possibility of an equatorward flux of ammonium, if nitrification is slow and N_2 is not lost to the atmosphere north of 36°25'N.

Further quantification of our present estimates are confounded, however, by seasonal and interannual variations of the sinking processes, by uncertainties in the amount of primary production and excretion of DOC, and by accurate assessment of spatio-temporal changes of DOM stocks. Reduced subduction beneath the Gulf Stream, increased coastal photosynthesis, reduced CDOC/DOC ratios, and increased release of DOC within coastal habitats from the marine food web and/or anthropogenic loadings would all favor (1) larger stocks of shelf DOC, and (2) a larger role of DOC in oxygen consumption within the deep sea. The opposite trends of these processes would lead to smaller stocks and roles of shelf DOC in global carbon cycles.

We do conclude that some shelf export of DOC, with a positive gradient between coastal and oceanic stocks, as well as falling particles, are required to balance carbon, nitrogen, and oxygen budgets of the North Atlantic, based on one snapshot of hydrographic properties [*Roemmich and Wunsch*, 1985]. Seasonal subduction, cabelling, and convection of surface waters may initiate annual storage, in sinking waters of the North Atlantic, of perhaps 0.9-1.2 x 10^{15} g DOC yr^{-1} (Table 1). Depending upon the different estimates of primary production and DOC stocks of coastal waters, the amount of DOM supplied by rivers and the shelf food web may constitute 29-43% of the proposed basin-wide sequestration of carbon and nitrogen.

The next generation of biophysical models involving satellite color imagery must improve upon more primitive ones [*Walsh et al.*, 1987; *Wroblewski et al.*, 1988; *Wroblewski*, 1989; *Ishizaka*, 1990; *Platt et al.*, 1991; *Gregg and Walsh*, 1992] by (1) first distinguishing between the dissolved and particulate components of the radiance signal, and (2) by providing resolution of the fates of the terrestrial and marine sources of CDOC. Future bio-optical research must now also focus on coastal waters of high and middle latitudes, as well as open ocean regimes, to provide eventual validation data, from follow-on satellite and aircraft color sensors, for our crude mathematical hypotheses of carbon and nitrogen cycling in the North Atlantic.

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